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**DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[Field of the Invention]

[0001]

This invention relates to a 1 liquid moisture curing nature constituent suitable as urethane system adhesives.

[Background of the Invention]

[0002]

Polyurethane resin is used for broad uses, such as adhesives, a coating material, a sealing material, flooring, an elastic paving material, and a water blocking material, by the outstanding adhesive property and pliability.

In such a use, the isocyanate group end prepolymer produced by making raw material polyol and an isocyanate compound react is contained, and the 1 liquid moisture curing type hardenability constituent which reacts to the moisture in air or a substrate to be pasted up, and is hardened is known. Using polyether polyol and polyester polyol is known as raw material polyol.

[0003]

If the polyether polyol which is an ordinary temperature fluid is used as raw material polyol, since a prepolymer serves as hypoviscosity, a hardenability constituent with sufficient workability will be obtained. However, when it is used for the adhesives applied to a building material, autoparts, and the film for food packing, and a water blocking material use, an adhesive property may be insufficient by the kind of substrate to be pasted up. For example, to the sheet made from polyvinyl chloride and the sheet made from aluminum which are used as flooring or wallpaper, an adhesive property is insufficient.

On the other hand, when the polyester polyol of an adipic acid system or a phthalate system is used as raw material polyol, the adhesive property to the sheet made from polyvinyl chloride or the sheet made from aluminum is excellent, but. In adipic acid system polyester polyol, since crystallinity is high, there is a problem in workability that it is easy to become a solid at ordinary temperature. In a 1 liquid moisture curing type, since moisture does not permeate the inside of resin easily, moisture curing nature becomes insufficient easily. In phthalate system polyester polyol, although there is no crystallinity, viscosity is very high, and since it becomes hyperviscosity further when it is considered as a prepolymer, a point [ need / a lot of solvents and plasticizers / to be used together ] is a problem.

[0004]

Then, the method of using together the polyether polyol which is hypoviscosity, and the polyester polyol which is excellent in an adhesive property is proposed. However, polyether polyol and polyester polyol have the problem of compatibility being bad and being easy to divide these mixtures into a bilayer.

Since reactivity differs between polyether polyol and polyester polyol mutually, when using these together, it is necessary to make them react to a polyisocyanate compound in two steps, and they need to pass through the complicated process of prepolymer-izing. Although the method of using together the prepolymer which uses polyester polyol, and the prepolymer which uses polyether polyol was also proposed, there is a problem which compatibility is poor and is separated.

The method of using for adhesives the polyester polyether block copolymer which added alkylene oxide to polyester polyol is proposed by the patent documents 1 and 2. However, since the polymer which consists of a block copolymerization chain of a polyester chain and a polyether chain is used, it is easy to condense and-izing cannot fully be carried out [ hypoviscosity ].

[Patent documents 1] The \*\* table No. 511532 [ 2003 to ] gazette

[Patent documents 2] JP,2004-143314,A

[Description of the Invention]

[Problem(s) to be Solved by the Invention]

[0005]

Thus, although it excels in an adhesive property and the hardenability constituent used for an adhesives use is expected for viscosity to be low, it is difficult to reconcile these. It is preferred that the breaking strength in a hardened material is large in order to obtain big adhesive strength, and in order to acquire good adhesion durability, it is preferred that the elongation of a hardened material is good.

The purpose of this invention is as follows.

Be made in order to solve the above-mentioned technical problem, and viscosity be low and excel in an adhesive property.

Provide a 1 liquid moisture curing nature constituent voltinism constituent with good breaking strength and elongation in a hardened material.

[Means for Solving the Problem]

[0006]

In order to attain the above-mentioned purpose, this invention is a 1 liquid moisture curing nature constituent which uses as a hardening component an isocyanate group end prepolymer produced by making the hydroxyl value 10 – polyol (A) and a polyisocyanate compound (B) of 300 mgKOH/g react, Said polyol (A) provides a 1 liquid moisture curing nature constituent by which polyester ether polyol (A1) produced by carrying out copolymerization of a polycarboxylic anhydride (b) and the alkylene oxide (c) being included to an initiator (a).

[Effect of the Invention]

[0007]

According to this invention, while viscosity is low and excelling in an adhesive property, a 1 liquid moisture curing nature constituent with good breaking strength and elongation in a hardened material is obtained.

[Best Mode of Carrying Out the Invention]

[0008]

[Initiator (a)]

It is preferred to use the compound which has 2–8 active hydrogen atoms per molecule as an initiator (a) used when manufacturing polyester ether polyol (A1). For example, a polyhydric alcohol class, polyamine, alkanolamines, and phenols are mentioned.

As a desirable example, ethylene glucol, a diethylene glycol, A polyethylene glycol, propylene glycol, dipropylene glycol, And dihydric alcohol, such as 1,4–butanediol; Trimethylolpropane, Tetravalent alcohols, such as trihydric alcohol; pentaerythritols, such as trimethylolethane and glycerin; Sorbitol, And the polyhydric alcohol class of 8 value alcohols, such as 6 value alcohols [, such as dipentaerythritol, ]; and sucrose, etc.; Ethylenediamine, Polyamine, such as hexamethylenediamine and tolylenediamine; phenols, such as alkanolamine; bisphenol A, such as monoethanolamine, propanolamine, and diethanolamine, are mentioned.

[0009]

These polyhydric alcohol classes, polyamine, and alkanolamines, The hydroxyl value conversion molecular weight per hydroxyl group produced by adding alkylene oxide to phenols can also use the polyether polyol (the hydroxyl value 37 – 374 mgKOH/g) of 150–1500 as an initiator (a).

The hydroxyl value conversion molecular weight per hydroxyl group can use polyoxy tetramethylen polyol, polyester polyol, polycarbonate polyol, etc. of 150–1500 (the hydroxyl value 37 – 374 mgKOH/g) as an initiator (a). What is produced by making carry out ring opening polymerization of the lactone monomer is mentioned by using as an initiator what is produced as this polyester polyol by making carry out the condensation reaction of a polyhydric alcohol class and the polyvalent carboxylic acid, and a polyhydric alcohol class.

The polyether polyol of 150–1500 (the hydroxyl value 37 – 374 mgKOH/g) has the preferred hydroxyl value conversion molecular weight per hydroxyl group which added alkylene oxide by using polyhydric alcohol or polyhydric alcohol as an initiator as an initiator (a). Especially this polyether polyol is preferred when it manufactures polyester ether polyol (A1), and using a composite metal cyanide complex catalyst as catalyst (x).

In this invention, the hydroxyl value conversion molecular weight of polyol says the value calculated using the following formula using the hydroxyl value measured by the method based on JIS K1557.

Hydroxyl value conversion molecular weight = (56100/hydroxyl value) the number of hydroxyl groups of x polyol.

[0010]

let the number of hydroxyl groups of polyester ether polyol (A1) be a thing which is in agreement with the number of active hydrogen atoms per molecule of an initiator (a) and which is been [ a thing / it ] rich and made. In this invention, it is more preferred to use the compound which has 2–3 active hydrogen atoms per molecule as the above-mentioned initiator (a), and, as for the number of hydroxyl groups of the polyester ether polyol (A1) in this invention, 2–3 are more preferred.

The using rate of an initiator (a) has [ 10 – 60 mass % ] preferably more preferred 1 – 60 mass % to the sum total of the charge of all the raw materials used for composition of polyester ether polyol (A1). The characteristic of an initiator appears that the using rate of an initiator (a) is more than the lower limit of a mentioned range, and the mechanical physical property of the hardened material produced by the prepolymer obtained since there is much quantity of the polycarboxylic anhydride in polyester ether polyol as it is below the upper limit of a mentioned range carrying out moisture curing, and an adhesive property are excellent.

[0011]

[Polycarboxylic anhydride (b)]

As a polycarboxylic anhydride (b) in this invention, phthalic anhydride, a maleic anhydride, a succinic anhydride, etc. are mentioned, for example. Since cohesive force and polarity are very high, especially an aromatic polycarboxylic anhydride is preferred in order to contribute to the adhesive property to various adherends greatly. Especially phthalic anhydride is preferred.

The using rate of the above-mentioned polycarboxylic anhydride (b) has preferred 5 – 50 mass % to the sum total of the charge of all the raw materials used for composition of polyester ether polyol (A1), and especially its 10 – 40 mass % is preferred. By making the above-mentioned using rate of a polycarboxylic anhydride (b) more than 10 mass %, the mechanical strength of a hardened material and adhesive property which are acquired by the prepolymer obtained carrying out moisture curing can be raised. The viscosity of the polyester ether polyol (A1) obtained can be low stopped by below 50 mass % carrying out.

[0012]

[Alkylene oxide (c)]

As alkylene oxide (c) which polymerizes an initiator (a) with a polycarboxylic anhydride (b), the alkylene oxide of the carbon numbers 2–4 is preferred. As an example, propylene oxide, 1,2–butylene oxide, 2,3–butylene oxide, ethylene oxide, etc. are mentioned. Alkylene oxide may use two or more sorts together, using only one sort. In this invention, use of ethylene oxide or propylene oxide is preferred, and especially use of only propylene oxide is preferred.

[0013]

As for the amount of the alkylene oxide (c) used, 50 / 50 – 95/5 are preferred to a polycarboxylic anhydride (b) at a mole ratio (c/b), and 50 / 50 – 80/20 are more preferred. It can stop that the unreacted material of a polycarboxylic anhydride (b) remains into polyester ether polyol (A1) by making the mole ratio of alkylene oxide (c) more than the lower limit of a mentioned range, and acid value of polyester ether polyol (A1) can be made low. The adhesive property of the hardened material produced by the prepolymer obtained carrying out moisture curing because below the upper limit of a mentioned range carries out, and mechanical strength are excellent.

[0014]

[Catalyst (x)]

Although the polyester ether polyol (A1) in this invention can be manufactured by carrying out addition condensation of a polycarboxylic anhydride (b) and the alkylene oxide (c) to the above-mentioned initiator (a), it is the point of increasing polymerization reaction speed, and it is preferred to use catalyst (x) for this polymerization reaction.

As this catalyst (x), a ring-opening-addition polymerization catalyst is used suitably. As an example, alkali catalyst; composite metal cyanide complex catalyst [ , such as a potassium hydrate and cesium hydroxide, ], a phosphazene catalyst, etc. are mentioned. Since polyester ether polyol (A1) with a smaller value of Mw/Mn is obtained, especially the thing for which a composite metal cyanide complex catalyst is used is preferred.

As a composite metal cyanide complex, what the organic ligand configurated in the zinhexacyano cobaltate complex is preferred. As an organic ligand, ether, such as ethyleneglycol dimethyl ether and diethylene glycol dimethyl ether, and alcohols like tert-butyl alcohol are preferred.

The using rate of catalyst (x) has [ 0.003 – 0.03 mass % ] preferably more preferred 0.0001 – 0.1 mass % to the polyester ether polyol (A1) which is output. There are few adverse effects of a residual catalyst that a polymerization takes place certainly that the using rate of catalyst (x) is more than the lower limit of a mentioned range, and it is below the upper limit of a mentioned range.

[0015]

[Polyester ether polyol (A1)]

Polyester ether polyol (A1) is preferably obtained to an initiator (a) under existence of catalyst (x) by carrying out copolymerization of a polycarboxylic anhydride (b) and the alkylene oxide (c).

Polyester ether polyol (A1) can be prepared by the following methods. Initiator (a), polycarboxylic anhydride (b), and catalyst (x) is first supplied to the reaction vessel beforehand, and it is made to react, adding alkylene oxide (c) there slowly. Since the direction of a polycarboxylic anhydride (b) has quick ring opening reaction in that case and does not carry out the continuation addition reaction of the polycarboxylic anhydride (b) from alkylene oxide (c) at it, A polycarboxylic anhydride (b) and the copolymer which has the copolymerization chain which 1 mol of alkylene oxide (c) added at a time by turns can be obtained.

The acid value of the polyester ether polyol (A1) obtained can be reduced by adding alkylene oxide (c) superfluously and making alkylene oxide (c) add to an end with a block. As for the acid value of polyester ether polyol (A1), 2.0 or less mgKOH/g may be preferred, its 1.0 or less mgKOH/g may be more preferred, and zero may be sufficient as it. Reactivity with an isocyanate is good in the acid value of polyester ether polyol (A1) being below the above-mentioned upper limit, and since the hydrolysis resistance of the hardened material in which the prepolymer obtained is obtained by carrying out moisture curing is excellent, it is desirable.

In polyester ether polyol (A1), the portion which a polycarboxylic anhydride (b) and 1 mol of alkylene oxide (c) have added at a time by turns, Since both ratio is constant, the whole structure is designed with the molecular weight of an initiator (a), and the addition amount of the alkylene oxide (c) of an end.

[0016]

A uniform mixture is not obtained even if it mixes the polymer produced by making the polymer produced by making phthalate system polyester polyol and a polyisocyanate compound react, and polyether polyol and a polyisocyanate compound react.

Compatibility is [ that it will be easy to dissociate if time passes even if mix polyester polyol and polyether polyol previously, a polyisocyanate compound is made to react to these mixtures and it prepolymer-izes ] insufficient.

[0017]

The hydroxyl value of polyester ether polyol (A1) has preferred 11 – 112 mgKOH/g, and especially its 22 – 80 mgKOH/g is preferred. That is, as for the hydroxyl value conversion molecular weight per hydroxyl group, it is preferred that it is 500–5000, and 700–especially 2500 are preferred. It becomes the thing excellent in the adhesive property to the substrate of the hardenability constituent obtained as the hydroxyl value conversion molecular weight per hydroxyl group is 500 or more to be pasted up. Hypoviscosity-ization of the hardenability constituent obtained as the hydroxyl value conversion molecular weight per hydroxyl group is 5000 or less can be attained.

Adjustment of the hydroxyl value conversion molecular weight of this polyester ether polyol (A1) can be easily performed by adjusting suitably the polycarboxylic anhydride (b) and the number of mols of alkylene oxide (c) which are polymerized to an initiator (a).

[0018]

As for polyester ether polyol (A1), it is preferred that the values (M') which divided the remaining molecular weight excluding the molecular weight of the initiator (a) from the hydroxyl value conversion molecular weight by the functional group number of the initiator (a) are 100–3000, and it is preferred that it is especially 200–1500.

Here, the above-mentioned "the value (M') which divided the remaining molecular weight excluding the molecular weight of the initiator from the hydroxyl value conversion molecular weight by the functional group number of the initiator" means the average molecular weight per [ which is formed of copolymerization of a polycarboxylic anhydride (b) and alkylene oxide (c) ] copolymerization chain.

The viscosity of the polyester ether polyol (A1) obtained as said value (M') is 3000 or less does not become high too much, and a

good adhesive property can be made to reveal that said value (M') is 100 or more. Adjustment of said value (M') can be easily performed by adjusting suitably the polycarboxylic anhydride (b) and the number of mols of alkylene oxide (c) which are polymerized to an initiator (a) like adjustment of the above-mentioned hydroxyl value conversion molecular weight.

Although the viscosity in particular at 60 °C of a prepolymer is not restricted, from a point of the spreading nature of a 1 liquid moisture curing nature constituent, its 20,000 or less mPa·s is preferred, and its range of 1,000 – 15,000 mPa·s is more preferred. The value of the viscosity in this specification is a value (unit: mPa·s) produced by measuring on 60 °C conditions by E type viscosity meter (east opportunity industrial company make: RE-80U model).

[0019]

[Polyol (A)]

The hydroxyl value in which polyol (A) contains the above-mentioned polyester ether polyol (A1) is [ 10 – 300 mgKOH/g, i.e., the hydroxyl value conversion molecular weight per hydroxyl group, ] the amount polyol of polymers of 187–5610.

The hydroxyl value of polyol (A) has preferred 11 – 112 mgKOH/g, and its 22 – 80 mgKOH/g is the most preferred. That is, 500–5000 have a preferred hydroxyl value conversion molecular weight per hydroxyl group, and 700–especially 2500 are preferred.

As for the content of the polyester ether polyol (A1) in the whole quantity of polyol (A), it is preferred that it is more than 30 mass %, and more than its 50 mass % is more preferred. It is most preferred that 100 mass % is polyether ether polyol (A1) substantially.

[0020]

As other polyols (A2) other than the above-mentioned polyester ether polyol (A1) contained in polyol (A), The number of active hydrogen atoms per molecule uses as an initiator the compound whose number is 2–8, The polyoxypropylene polyol produced by carrying out the ring-opening-addition polymerization of the alkylene oxide, Polyoxyethylene polyol, Polyoxy ethylene propylene polyol; The polyester polyol; polyhydric alcohol class acquired by making carry out the condensation reaction of a polyhydric alcohol class and the polyvalent carboxylic acid is used as an initiator. Polyester polyol; polyoxy tetramethylen polyol produced by making carry out ring opening polymerization of the lactone monomer; polycarbonate polyol etc. are mentioned. As for the polyol (A2) of these others, it is preferred that it is number of hydroxyl groups 2–8 piece polyol, and its 2–3 polyols are preferred. The hydroxyl value of other polyols (A2) has preferred 10 – 300 mgKOH/g, its 11 – 112 mgKOH/g is more preferred, and especially its 22 – 80 mgKOH/g is preferred. Namely, especially 700–2500 with a hydroxyl value conversion molecular weight preferred [ 187–5610 ] per hydroxyl group, and more preferred 500–5000 are preferred.

As for the content of other polyols (A2) in the whole quantity of polyol (A), it may be preferred that it is below 70 mass %, below its 50 mass % may be more preferred, and zero may be sufficient as it.

[0021]

[Polyisocyanate compound (B)]

The polyisocyanate compound (B) (it may only be called polyisocyanate (B).) which can be used in this invention, Although not limited in particular, for example Diphenylmethane diisocyanate, polyphenylene polymethylene polyisocyanate, Aromatic polyisocyanate compounds, such as 2, 4-tolylene diisocyanate and 2, 6-tolylene diisocyanate; Xylylene diisocyanate, Aromatic polyisocyanate compounds, such as meta-tetramethyl xylenediisocyanate; Hexamethylene di-isocyanate, aliphatic polyisocyanate compound [ such as 2,2,4-trimethyl hexamethylene di-isocyanate, ]; -- alicycle fellows polyisocyanate compound [ such as isophorone diisocyanate and 4,4'-methylenebis (cyclohexylisocyanate), ]; -- and, The urethane denaturation object acquired from said polyisocyanate compound, a buret denaturation object, an allophanate denaturation object, a carbodiimide denaturation object, an isocyanurate denaturation object, etc. are mentioned.

Since excelling in reactivity with polyol (A) and the viscosity of a 1 liquid moisture curing nature constituent obtained become low easily, as a polyisocyanate compound (B), aromatic diisocyanate and these denaturation objects are preferred. Diphenylmethane diisocyanate, polyphenylene polymethylene polyisocyanate, 2, 4-tolylene diisocyanate and 2, 6-tolylene diisocyanate, and these denaturation objects are especially preferred.

A polyisocyanate compound (B) may use one sort independently, and may use two or more sorts together.

[0022]

[Prepolymer]

The isocyanate group end prepolymer in this invention is obtained by making a polyisocyanate compound (B) react to polyol (A). This isocyanate group end prepolymer is obtained by making the above-mentioned polyol (A) and a polyisocyanate compound (B) react so that the mole ratio (an isocyanate group/hydroxyl group) to the hydroxyl group of an isocyanate group may be set to 1.3–10.0. These mole ratios are 1.8–7.0 more preferably. The viscosity of the prepolymer generated as this mole ratio is more than [ less than 1.3 ] does not become high too much, and is preferred in respect of workability and moisture curing nature. By using 10.0 or less, there is little survival of an unreacted polyisocyanate compound (B), and the mechanical physical property of the hardened material of the hardenability constituent obtained eventually becomes good.

It is preferred that isocyanate group \*\*\*\*\* in an isocyanate group end prepolymer is 0.5 to 20 mass %, it is more preferred that it is one to 15 mass %, and especially 1 – 12 mass % is preferred. Viscosity does not become it high that this isocyanate group content is more than 0.5 mass % too much, and it is desirable in respect of workability and moisture curing nature. With it being below 20 mass %, there is little survival of an unreacted polyisocyanate compound and the mechanical physical property of the hardened material of the hardenability constituent obtained eventually becomes good.

[0023]

[1 Liquid moisture curing nature constituent]

The 1 liquid moisture curing nature constituent of this invention the isocyanate group end prepolymer produced by making a polyisocyanate compound (B) react to polyol (A), It is considered as the hardening component hardened by a reaction with moisture, moisture curing of this hardening component is carried out, and it is made to harden without using a chain extension agent or

hardening agents, such as low-molecular-weight polyol and polyamine.

The 1 liquid moisture curing nature constituent of this invention can be manufactured under the conditions into which moisture does not go, and can be put in and saved at a well-closed container, and it can take out from a container at the time of use, can apply to a substrate, and can be made to harden by putting into the atmosphere by making the isocyanate group in the moisture (humidity) in the air, and a hardening component react.

Although the manufacturing method in particular of the 1 liquid moisture curing nature constituent of this invention is not limited, it is good to add various additive agents [ above / desirable essential ingredient and if needed ], to knead enough using agitating devices, such as a mixed mixer, under decompression or a nitrogen atmosphere, to make it distribute uniformly, and to consider it as a constituent.

[0024]

[Additive agent]

As an additive agent added by the 1 liquid moisture curing nature constituent of this invention if needed, the following are mentioned, for example.

(Curing catalyst)

As a curing catalyst, the publicly known catalyst which promotes a urethane-ized reaction and an urea reaction can be used, for example, organic acid tin, organic acid lead, etc., such as tertiary amine compounds, such as triethylamine, dibutyltin dilaurate, dioctyl tin maleate, and 2-ethylhexanoic acid tin, are mentioned.

[0025]

( Plasticizer)

As a plasticizer, dioctyl phthalate, dibutyl phthalate, phthalic acid diisononyl ester, Dioctyl adipate, diisononyl adipate, succinic acid isodecyl, butyl oleate, tricresyl phosphate, adipic acid propylene glycol polyester, rice-bran oil fatty acid ester, etc. are mentioned.

[0026]

( Solvent)

The 1 liquid moisture curing nature constituent of this invention may be made to contain a solvent. For the adhesives use for food packaging films, use of a solvent is especially preferred.

As a solvent which can be used, aliphatic hydrocarbon; ethyl acetate, such as isoparaffin and a mineral spirit, Acetate ester, such as butyl acetate; amide, such as aromatic hydrocarbon; dimethylformamides, such as ketone; toluene, such as methyl ethyl ketone and methyl isobutyl ketone, and xylene, is mentioned.

Since the 1 liquid moisture curing nature constituent of this invention can carry out [ hypoviscosity ]-izing by using specific polyester ether polyol (A1), even if a solvent is used for it, good viscosity is obtained by a little use. Use of a weak solvent is also possible.

[0027]

( Filler)

A filler can be blended with the 1 liquid moisture curing nature constituent of this invention if needed. By blending a filler especially in adhesion uses, such as adhesives for building materials, a coating material, a sealing material, an elastic paving material, and a water blocking material, in order that stand and it becomes difficult to hang down even in a field, and coverage may be uniform, and may be stabilized and an adhesive property may be stable, it is desirable. As an example of a filler, calcium carbonate, titanium oxide, magnesium carbonate, magnesium oxide, magnesium hydroxide, iron oxide, a zinc oxide, barium oxide, zinc carbonate, carbon black, silica, diatomite, etc. are mentioned. The amount of the filler used has preferred 0 - 60 mass % among a hardenability constituent (100 mass %), and its 0 - 50 mass % is preferred. By below 60 mass % carrying out, the coating operability of adhesives is good.

[0028]

(In addition to this auxiliary agent)

A thixotropic grant agent, an antioxidant, an ultraviolet ray absorbent, paints, a defoaming agent, fire retardant, an adhesion grant agent, etc. can be used if needed.

As a thixotropic grant agent, particle calcium carbonate, Aerosil (Japanese Aerosil Co. article), aliphatic series amide, hydrogenation castor oil, etc. are mentioned.

As an antioxidant, butylhydroxytoluene (BHT), butylhydroxyanisole (BHA), diphenylamine, a phenylenediamine, phosphorous acid triphenyl, etc. are mentioned.

As an ultraviolet ray absorbent, a hindered phenol system, a benzotriazol system, a hindered amine system, etc. are mentioned.

There are an inorganic pigment and an organic color in paints, and a titanium dioxide, a zinc oxide, ultramarine, red ocher, lithopone, lead oxide, a cadmium sulfide, cobalt oxide, an aluminum oxide, etc. can be used as an inorganic pigment. An azo pigment, a copper phthalocyanine pigment, etc. are mentioned as an organic color.

A polysiloxane compound etc. are mentioned as a defoaming agent.

As fire retardant, chloro alkyl phosphate, dimethylmethyl phosphate, ammonium poly phosphate, neopentyl star's picture polyether, bromination polyether, bromine, and phosphorus compounds can be used.

As an adhesion grant agent, terpene resin, phenol resin, rosin resin, and xylene resin can be used.

[0029]

Since the 1 liquid moisture curing nature constituent of this invention is hypoviscosity as shown in the below-mentioned example, its workability is good. The peel strength after adhesion is high, and while excelling in an adhesive property, the breaking strength and elongation in a hardened material are good. And it is possible to use for the adhesion use to an extensive material.

As a substrate to be pasted up, it can be used for wide range materials, such as resin material; concretes, such as metallic material; polyamide, such as aluminum, iron, copper, etc. besides wood, polyethylene terephthalate, nylon, and polypropylene, asphalt, and a stone. Among these substrates to be pasted up, resin, such as wood; aluminum; polyamide and polyethylene terephthalate, is

preferred, and it excels especially in the adhesive property with aluminum.

[Example]

[0030]

Hereafter, an example is shown and this invention is explained concretely. However, this invention is not limited to the following examples.

<Use raw material>

The polyol used as a raw material in the following examples is [ following ] a passage. A molecular weight is a hydroxyl value conversion molecular weight.

– PPG-1000 (abbreviation) : hydroxyl value 112 mgKOH/g, polyoxypropylene diol of the molecular weight 1000 which were manufactured using the KOH catalyst using propylene glycol as an initiator.

– PPG-2000 (abbreviation) : hydroxyl value 56 mgKOH/g, polyoxypropylene diol of the molecular weight 2000 which were manufactured using the KOH catalyst using propylene glycol as an initiator.

– PBA (abbreviation) : hydroxyl value 56 mgKOH/g, poly (butylenediol) horse mackerel peat diol of the molecular weight 2000, Japanese polyurethane industrial company make, the trade name N-4010.

– IP/MPD (abbreviation) : hydroxyl value 56 mgKOH/g, poly (3-methyl pentanediol) isophthalate diol of molecular weight 2000\*\*, the Kuraray Co., Ltd. make, the trade name P-2030.

[0031]

[Manufacture of example of manufacture 1:polyester etherdiol (A1-1)]

In the resisting pressure reactor provided with the agitator and the nitrogen introducing pipe, 1000 g of PPG-1000 which is polyether polyol as an initiator (a) was supplied. Subsequently, as a polycarboxylic anhydride (b), 400 g (2.70 mol) of phthalic anhydride was supplied in the above-mentioned reaction vessel, and was agitated. Subsequently, 0.2 g of a zinhexacyano cobaltate tert-butyl alcohol complex compound catalyst is supplied as catalyst (x), and it was made to react for 7 hours, adding 600 g (10.3 mol) of propylene oxide slowly as alkylene oxide (c) at 130 \*\* under a nitrogen atmosphere. Then, after checking that the fall of reaction vessel internal pressure has stopped, output is extracted from a reaction vessel, The polyester etherdiol (A1-1) (hydroxyl value 56.3 mgKOH/g) to which phthalic anhydride and propylene oxide polymerized at the end of PPG-1000 which is polyether polyol was obtained. From the measurement result of <sup>1</sup>H-NMR of this polyester etherdiol, it was checked that this diol (A1-1) has phthalic anhydride and a polymerization chain of propylene oxide.

As for the hydroxyl group conversion molecular weight per hydroxyl group of the polyester etherdiol (A1-1) obtained by this example, 496 and the acid value of 996 and "the value (M') for which the remaining molecular weight excluding the molecular weight of the initiator from the hydroxyl value conversion molecular weight was divided by the functional group number of the initiator" were 0.11.

[0032]

[Manufacture of example of manufacture 2:polyester etherdiol (A1-2)]

In the example 1 of manufacture, the amount of the phthalic anhydride used was changed into 600 g (4.05 mol), and the amount of the propylene oxide used was changed into 400 g (6.90 mol). Others obtained the polyester etherdiol (A1-2) (hydroxyl value 57.6 mgKOH/g) to which phthalic anhydride and propylene oxide polymerized at the end of PPG-1000 like the example 1 of manufacture.

From the measurement result of <sup>1</sup>H-NMR of this polyester etherdiol, it was checked that this diol has phthalic anhydride and a polymerization chain of propylene oxide.

As for the hydroxyl group conversion molecular weight per hydroxyl group of the polyester etherdiol (A1-2) obtained by this example, 474 and the acid value of 974 and "the value (M') for which the remaining molecular weight excluding the molecular weight of the initiator from the hydroxyl value conversion molecular weight was divided by the functional group number of the initiator" were 0.14.

[0033]

[Manufacture of an example 1:1 liquid moisture curing nature constituent]

757 g of the polyester etherdiol (A1-1) obtained in the example 1 of manufacture in the reaction vessel provided with the agitator and the nitrogen introducing pipe, 243 g of 4,4'-diphenylmethane diisocyanate (it is [ Japanese polyurethane industrial company make, trade name millimeter ONETO MT, and isocyanate group content 33.6 mass % and the following ] the same.) was taught as a polyisocyanate compound (B), and it was made to react at 80 \*\* under a nitrogen atmosphere for 4 hours. The isocyanate group/hydroxyl group (mole ratio) was 2.56.

Take out some contents after a reaction and isocyanate group (it may abbreviate to NCO hereafter.) content is measured, It checked that it was below the content calculated theoretically, the reaction was suspended and extracted, and NCO content 4.95 mass % and the isocyanate group end prepolymer of the viscosity 3,300 (mPa-s) in 60 \*\* were obtained. This was used as a 1 liquid moisture curing nature constituent.

[0034]

[Manufacture of an example 2:1 liquid moisture curing nature constituent]

In Example 1, it changed into the polyester etherdiol (A1-2) which obtained polyester etherdiol (A1-1) in the example 2 of manufacture, and also the isocyanate group end prepolymer was obtained like Example 1. The isocyanate group/hydroxyl group (mole ratio) was 2.50.

The viscosity in 4.87 mass % and 60 \*\* of the NCO content of the obtained isocyanate group end prepolymer was 11,000 (mPa-s). This was used as a 1 liquid moisture curing nature constituent.

[0035]

[Manufacture of an example 3:1 liquid moisture curing nature constituent (additive agent content)]

The additive agent was added to the isocyanate group end prepolymer obtained in Example 1, and the 1 liquid moisture curing nature constituent was manufactured.

To namely, 430 g of the isocyanate group end prepolymer obtained in Example 1. As a plasticizer, as 50 g of diisononyl phthalate, and a solvent 70 g of toluene, what added and kneaded 400g of heavy calcium carbonate (: by a Shiraishi industrial company -- NS-the same [ 400 or less .]) and 50 g of particle composition calcium carbonate (Shiraishi industrial company make: the same [ below Hakuenka CCR ]) as a filler was used as a 1 liquid moisture curing nature constituent.

[0036]

[Manufacture of an example 4:1 liquid moisture curing nature constituent (additive agent content)]

What added and kneaded the same additive agent as Example 3 to 430 g of isocyanate group end prepolymers obtained in Example 2 was used as a 1 liquid moisture curing nature constituent.

[0037]

[Manufacture of an example 5:1 liquid moisture curing nature constituent (additive agent content)]

In Example 1, the amount of the polyester etherdiol (A1-1) used was changed into 624 g, and the amount of the 4 and 4'-diphenylmethane diisocyanate used was changed into 376 g. Others obtained the isocyanate group end prepolymer like Example 1. The isocyanate group/hydroxyl group (mole ratio) was 4.83. The NCO content of the obtained isocyanate group end prepolymer was the viscosity 1,800 (mPa-s) in 9.92 mass % and 60 \*\*.

What added and kneaded the same additive agent as Example 3 to 430 g of the obtained prepolymer was used as a 1 liquid moisture curing nature constituent.

[0038]

[Manufacture of an example 6:1 liquid moisture curing nature constituent (additive agent content)]

In Example 2, the amount of the polyester etherdiol (A1-2) used was changed into 622 g, and the amount of the 4 and 4'-diphenylmethane diisocyanate used was changed into 378 g. Others obtained the isocyanate group end prepolymer like Example 2. The isocyanate group/hydroxyl group (mole ratio) was 4.74. The NCO content of the obtained isocyanate group end prepolymer was the viscosity 6,000 (mPa-s) in 9.90 mass % and 60 \*\*.

What added and kneaded the same additive agent as Example 3 to 430 g of obtained prepolymers was used as a 1 liquid moisture curing nature constituent.

[0039]

[Comparative example 1]

Instead of polyester ether polyol (A1), the 1 liquid moisture curing nature constituent was prepared using polyether polyol without an ester group.

That is, in Example 1, polyoxypropylene diol (PPG-2000) was used instead of the polyester etherdiol (A1-1) obtained in the example 1 of manufacture, and also the isocyanate group end prepolymer was obtained like Example 1. The isocyanate group/hydroxyl group (mole ratio) was 2.57. The NCO content of the obtained isocyanate group end prepolymer was the viscosity 850 (mPa-s) in 4.96 mass % and 60 \*\*. This was used as a 1 liquid moisture curing nature constituent.

[0040]

[Comparative example 2]

Instead of polyester ether polyol (A1), adipic acid system polyester polyol was used and the 1 liquid moisture curing nature constituent was prepared.

That is, in Example 1, poly (butylenediol) horse mackerel peat diol (PBA) was used instead of the polyester etherdiol (A1-1) obtained in the example 1 of manufacture, and also the isocyanate group end prepolymer was obtained like Example 1. The isocyanate group/hydroxyl group (mole ratio) was 2.57. The NCO content of the obtained isocyanate group end prepolymer was the viscosity 10,000 (mPa-s) in 4.90 mass % and 60 \*\*. This was used as a 1 liquid moisture curing nature constituent.

[0041]

[Comparative example 3]

Instead of polyester ether polyol (A1), phthalate system polyester polyol was used and the 1 liquid moisture curing nature constituent was prepared.

That is, in Example 1, poly (3-methyl pentanediol) isophthalate diol (IP/MPD) was used instead of the polyester etherdiol (A1-1) obtained in the example 1 of manufacture, and also the isocyanate group end prepolymer was obtained like Example 1. The isocyanate group/hydroxyl group (mole ratio) was 2.57. The NCO content of the obtained isocyanate group end prepolymer was the viscosity 25,000 (mPa-s) in 4.98 mass % and 60 \*\*. This was used as a 1 liquid moisture curing nature constituent.

[0042]

[Comparative example 4]

Instead of polyester ether polyol (A1), the mixture of phthalate system polyester polyol and polyether polyol was used, and the 1 liquid moisture curing nature constituent was prepared.

That is, 379 g of IP/MPD and 378 g of PPG-2000 were supplied in the reaction vessel provided with the agitator and the nitrogen introducing pipe, it mixed, 243 g of further 4 and 4'-diphenylmethane diisocyanate was taught, and it was made to react at 80 \*\* under a nitrogen atmosphere for 4 hours. The isocyanate group/hydroxyl group (mole ratio) was 2.57. Some contents after a reaction were taken out, NCO content was measured, it checked that it was below the content calculated theoretically, the reaction was suspended and extracted, and NCO content 4.99 mass % and the isocyanate group end prepolymer of the viscosity 5,500 (mPa-s) in 60 \*\* were obtained. This was used as a 1 liquid moisture curing nature constituent.

[0043]

<Evaluation>

[Physical properties of a hardened material (film)]

The 1 liquid moisture curing nature constituent obtained by the above-mentioned example and the comparative example is applied so

that it may become 500 micrometers of thickness by an applicator on a biaxial stretched polypropylene film (OPP film), on 20 \*\* and the conditions of 60% of relative humidity, it was recuperated for one week and moisture curing was carried out. The dumbbell cutter cut the obtained film to specified shape, it stripped from the OPP film, the specimen was created, and the following physical-properties measurement was performed.

Each physical properties of 100% of elongation o'clock of a modulus of elasticity in tension (100%M, unit:MPa), 300% of elongation o'clock of a modulus of elasticity in tension (300%M, unit:MPa), \*\*\*\* breaking strength (Ts, unit:MPa), and elongation after fracture (E, unit:%) were measured. Based on JIS-K7311, using a tension tester as measuring equipment, the physical-properties measuring condition used the dumbbell No. 3 as the specimen, and performed it on condition of for speed-of-testing/of 200 mm.

A measurement result is shown in Table 1.

[0044]

[An adhesive examination]

According to JIS K-6833, the cement test of the 1 liquid moisture curing nature constituent was done by the following methods.

(Test sample creation)

The 1 liquid moisture curing nature constituent was applied to the position of 25 mm x 25 mm of end parts of the woody plywood (it is hereafter called plywood for short.) of 25-mm width x100-mm length x4-mm thickness in the spatula so that it might become a thickness of 0.2 mm. On this application portion, 25 mm x 25 mm of end parts of the aluminum plate manufacturing (it is called aluminum for short below.) of 25-mm width x100-mm length x2-mm thickness, It carried so that the other end of plywood and the other end of aluminum might counter mutually on both sides of said application portion, and it pushed lightly by hand, and fixed with the jig further at the time of \*\* at the time of \*\*. On 23 \*\* and the conditions of 50% of relative humidity, it is recuperated for one week, this was stiffened, and the test sample was obtained.

(Friction test)

About the obtained test sample, shear peel strength (unit: N/m<sup>2</sup>) was measured on condition of speed-of-testing 50 mm/min using the tension tester (made in Oriental Bawdwin, a product name: tensilon VTM-III-200). The result is shown in Table 1.

Viewing observed and estimated the desquamative state after exfoliation. A result is shown in Table 1. In Table 1, "AF" shows interfacial peeling. "AL (numerical value)" expresses a desquamative state with the rate of area, for example, "AL80 shows that 80% of the whole surface products of an adhesion part exfoliated in the interface of aluminum and a hardenability constituent, and 20% exfoliated in the interface of plywood and a hardenability constituent. The value of the rate of this area in Table 1 is average value when the friction test same about three test samples is done.

[0045]

[Table 1]



	一液硬化性 組成物の 粘度 (mPa・s)	フィルムの物性				接着性 (ベニヤ/Al)	
		100M (MPa)	300M (MPa)	Ts (MPa)	E (%)	せん断剥離 強度 (N/m <sup>2</sup> )	剥離状態
実施例 1	3,300	2.0	3.7	42.0	670	17.2 × 10 <sup>5</sup>	AF AL90
実施例 2	11,000	2.9	9.3	65.3	520	25.7 × 10 <sup>5</sup>	AF AL90
実施例 3	—	—	—	—	—	18.4 × 10 <sup>5</sup>	AF AL80
実施例 4	—	—	—	—	—	21.4 × 10 <sup>5</sup>	AF AL70
実施例 5	—	—	—	—	—	20.1 × 10 <sup>5</sup>	AF AL80
実施例 6	—	—	—	—	—	27.8 × 10 <sup>5</sup>	AF AL70
比較例 1	850	2.2	2.8	9.1	1,100	7.9 × 10 <sup>5</sup>	AF AL100
比較例 2	10,000	—	—	23.6	80	15.0 × 10 <sup>5</sup>	AF AL100
比較例 3	25,000	—	—	38.4	10	18.5 × 10 <sup>5</sup>	AF AL100
比較例 4	5,500 (分離)	—	—	—	—	—	—

[0046]

The film produced by being easy to use the 1 liquid moisture curing nature constituent of Examples 1 and 2 which consist of a prepolymer concerning this invention by hypoviscosity, and hardening this constituent is excellent in elongation, and its breaking strength is also better than the result of Examples 1 and 2 and the comparative examples 1-4. Shear peel strength is highly excellent also in the adhesive property.

On the other hand, the comparative example 1 which consists of a prepolymer prepared using polyether polyol is inferior to the breaking strength of a film, and an adhesive property, although viscosity is low and the elongation of a film is good.

The comparative examples 2 and 3 which consist of a prepolymer prepared using polyester polyol are inferior in the elongation and breaking strength of a hardened material (film) of what has a good adhesive property. If the elongation of a film is not good, when a heat shrinkage rate uses for the lamination of mutually different adherend, it will be easy to produce peeling.

The constituent of the comparative example 4 which consists of a prepolymer prepared using the mixture of polyether polyol and polyester polyol, When it was neglected, liquid dissociated, and a uniform film was not obtained, even if it applied so that it might become 500 micrometers of thickness by an applicator on a biaxial stretched polypropylene film (OPP film). For this reason, film properties and adhesive evaluation were not performed in the comparative example 4.

[0047]

If additive agents, such as calcium carbonate, are blended like Examples 3-6, while being able to give the characteristics, such as lappet prevention, the cost cut of a product can be aimed at. In Examples 3-6, even if it adds an additive agent, the shear strength is

high, an adhesive property is good, and it was accepted that it is satisfactory practically as adhesives. Since it would become non-Newtonian fluid and measurement of viscosity would be impossible if calcium carbonate is added, measurement of viscosity was not performed.

[Industrial applicability]

[0048]

the 1 liquid moisture curing nature constituent of this invention can be used for the use as which it is suitable for an adhesion use, and a good adhesive property with substrates, such as adhesives, a coating material, a sealing material, an elastic paving material, or a water blocking material, is specifically required -- it is desirable.

Since it excels in the adhesive property over wood, metal (especially aluminum), and resin, it is suitable for the adhesives in the lamination of adhesives [ of the adhesives; autoparts of a building material ];, a food packaging film, etc., etc.

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[Translation done.]